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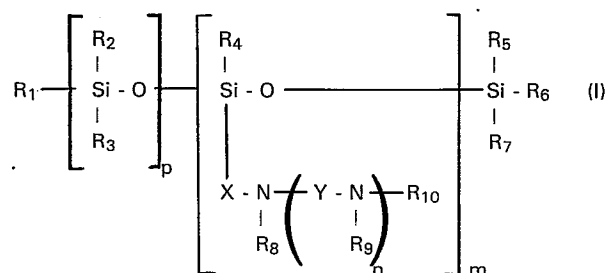
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(54) **Lubricating agents for use in the production of carbon yarns.**

(57) Lubricating agents for use in the production of carbon yarns comprise at least one amino polysiloxane of formula (I)



(where X represents an alkylene group with 3 to 5 carbon atoms, Y represents an alkylene group with 2 to 6 carbon atoms or a phenylene group, R₁ and R₃ each represent a hydrogen atom, an alkyl group with 1 to 5 carbon atoms or a phenyl group, R₂ and R₄ each represent a methyl group or an ethyl group, R₅, R₆ and R₇ each represent a hydrogen atom, a methyl group or an ethyl group, m is 1, n is an integer equal to or greater than 1 and p is 0 or an integer in the range of 1 to 5), as effective component, the nitrogen content of said effective component being 1 weight % or less. Such lubricating agents supply to the processed yarns superior filament separability and infusibility characteristics.

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Lubricating Agents for use in the Production
of Carbon Yarns

Background of the Invention

5 This invention relates to lubricating agents for the
production of carbon yarns and more particularly to
lubricating agents having specified amino polysiloxanes
as effective component. When applied to acrylic fibers
or carbon fibers derived from pitchy material to be used
as a precursor for the infusibilizing process
10 (hereinafter to be referred simply as precursor), these
agents can not only give to the precursor a superior
filament separability and processability, but also
prevent adhesion after the infusibilizing process, thus
making it possible to produce carbon yarns with superior
15 physical characteristics.

Carbon yarns are generally produced by first
obtaining non-flammable yarns from a precursor by a
process (hereinafter referred simply as the
infusibilizing process) wherein the precursor is heated
20 and burnt at 200 - 300°C in an oxidizing atmosphere;
and second by a carbonization process wherein
carbonization takes place in an inert atmosphere at a
high temperature, e.g. over 700°C. In such a case, a

lubricating agent is applied prior to the infusibilizing process, and usually during the process in which the precursor itself is produced. In addition to the generally desired characteristics such as lubricity,
5 antistatic capability and cohesion, however, it is important, in view of the aforementioned processes for the production of carbon yarns, that the lubricating agent to be used for this purpose be superior to providing a good filament separability and infusibility.

10 In the past, various substances, including phosphates of alkali metals, various cationic activators, polyoxyalkylene ether, etc., have been used as lubricating agents of this type. Although they are generally acceptable regarding antistatic capability,
15 cohesion and lubricity, they are inferior regarding their filament separability because of their basic tendency to become decomposed. In addition, they have the disadvantage of generating tar during the infusibilizing process or of vaporizing mostly during
20 the initial heating period and causing adhesion between the fibers.

In order to overcome this difficulty, many silicone-type lubricating agents have been considered such as dimethyl polysiloxanes, phenylmethyl
25 polysiloxanes, epoxy polysiloxanes, polyether

polysiloxanes, amino polysiloxanes, etc. (Japanese Patents Tokko 51-12739, Tokko 52-24136, Tokkai 52-148227, etc.). These silicone-type lubricating agents, however, have various disadvantages. Dimethyl polysiloxanes and phenylmethylpolysiloxanes are thermally superior but provide poor filament separability in the precursor and are poor in prevention of adhesion in the infusibilizing process. This may be because they do not contain polar groups in their molecules and hence their orientation (hereinafter used to mean the characteristic of uniform adhesion) regarding the precursor is insufficient. Moreover, since they are non-polar, problems of fuzz and yarn breakage caused by static electricity can occur easily.

Epoxypolysiloxanes tend to cause fiber-to-fiber fixing due, for example, to the ring-opening polymerization of epoxy groups within their molecules and since they themselves generate tar, they are totally incapable of preventing mutual adhesion during the infusibility process. Their presence, therefore, makes the problem worse instead of solving it. As for polyether polysiloxanes, the ether bonds within their molecules are thermally weak so that they mostly become decomposed and diffuse away, failing to exercise their capability of preventing adhesion. Moreover, their heat of thermal decomposition becomes a cause of abnormal reactions involving the yarns.

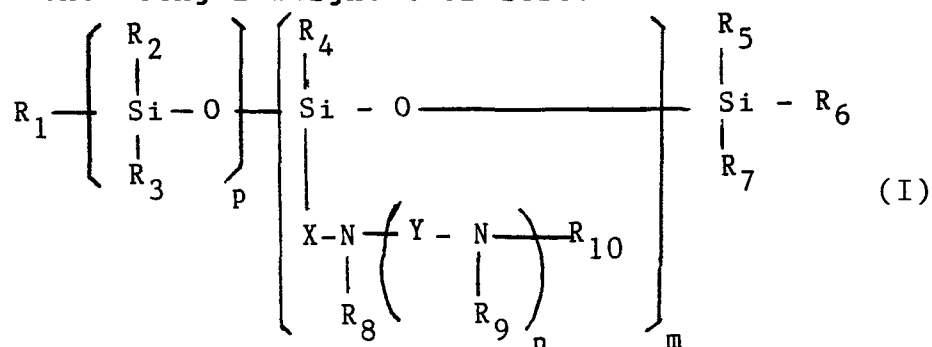
Amino polysiloxanes of the type proposed in the past, although they have more favorable characteristics than the other conventional silicone type lubricating agents discussed above have only one nitrogen atom per amino-modified group within their molecules and this means that only weak polar groups are loosely distributed around. Accordingly their orientation capability with respect to the precursor is inferior and the filament separability and degree of adhesion prevention they provide are not sufficient to be satisfactory.

It is therefore an object of this invention to eliminate the aforementioned disadvantage by providing lubricating agents which are superior in processability and opening property of each filament in the subsequent processes, including the production of precursors and the infusibilizing process, without causing problems such as adhesion, and thus make it possible to produce high quality carbon yarns.

The above and the other objects of the present invention have been achieved by the present inventors with the discovery that good lubricating agents for this purpose have as an effective component amino polysiloxanes with specific amino-modified groups of a certain nitrogen content.

Detailed Description of the Invention

According to this invention there is provided a lubricating agent for the production of carbon yarns characterised by comprising at least one amino polysiloxane of the general formula (I) as an effective component, the nitrogen content of said effective component being 1 weight % or less:



where X represents an alkylene group with 3 to 5 carbon atoms, Y represents an alkylene group with 2 to 6 carbon atoms or a phenylene group, R₁ and R₆ represent methyl, ethyl or hydroxyl groups, R₂ represents a hydrogen atom, an alkyl group with 1 to 5 carbons or a phenyl group, R₃, R₄, R₅ and R₇ each represent a methyl group or phenyl group, R₈, R₉ and R₁₀ each present a hydrogen atom, a methyl group or an ethyl group, m and p are each an integer equal to or larger than 1, and n is an integer in the range of 1 to 5.

Amino polysiloxanes of formula (I) may be obtained, for example, by condensation of a silane containing an amino group and a cyclic diorgano polysiloxane. In this

situation, both a single system of amino polysiloxanes shown by (I) and a mixed system of aforementioned amino polysiloxane and a polysiloxane-type compound corresponding to $m = 0$ in (I) can be obtained, depending
5 on the molar ratio between silane containing the amino group and the cyclic diorgano polysiloxane. Both these systems contain amino polysiloxanes shown by (I) as effective component and hence are lubricating agents according to the present invention but it is a
10 requirement that the nitrogen content of said effective component be 1 weight % or less. If the nitrogen content of the effective component exceeds 1 weight %, the orientation characteristic regarding the precursor becomes improved but the heat resistance becomes worse
15 and tar comes to be generated during the infusibilizing process so the ability to prevent adhesion is significantly affected. The viscosity of the effective component at 25°C should preferably be 100 to 10,000 cst (centistokes) and its nitrogen content should preferably
20 be 0.5 weight % or less. This is chiefly in anticipation of situations where diffusion may lower the capability of preventing adhesion and an increase in viscosity may adversely affect lubricity. In these cases, however, good results can generally be obtained
25 if a mixed system of the aforementioned type is used.

The lubricating agents of the present invention may

be used together with any known lubricant, softening agent, antistatic agent, surface active agent, antioxidant, antiseptic or conventional lubricating agent for the production of carbon yarns, as long as the
5 desired effects of the present invention are not adversely affected. There is no limitation on the amount of the aforementioned effective component to be contained, but it should preferably be 40 weight % or greater in view of the required filament separability of
10 the precursor and the required adhesion-preventing property during the infusibilizing process.

The lubricating agents of the present invention are applied during the precursor production process or before the infusibilizing process. As for the mode of
15 application, they may be applied either as an emulsion, as a solution with an organic solvent or straight. The may be applied by a kiss-roll method, a spray method or a guide-oiling method. The amount to be deposited in these cases is preferably 0.01 to 5 weight % with
20 respect to the precursor in order to obtain the required effects fully but economically.

As explained above, the lubricating agents of the present invention containing amino polysiloxanes shown by (I) as the effective component have a superior
25 processability in the precursor production process and

the infusibilizing process and in particular provide superior filament separability in the precursor and a superior capability of preventing adhesion in the infusibilizing process so that they can show better results than the previously proposed types of amino polysiloxanes. It is not clear why this result is obtained, but amino polysiloxanes of the present invention have two or more nitrogen atoms per amino-modified group within their molecules while there is only one nitrogen atom per amino-modified group of the molecules of amino polysiloxanes of the conventional type. It may be concluded because of this difference that there are strong polar groups concentrated in the case of amino polysiloxanes of the present invention while aminosiloxanes of the conventional type have loosely distributed weak polar groups. In other words, aminosiloxanes of the present invention are more strongly oriented with respect to the precursor and it seems that the extent of this orientation property becomes particularly important when the nitrogen content is reduced in view of the required heat resistance characteristics.

The following test examples are described by way of illustration of the present invention and its effects and do not comprise a limiting definition of the present invention.

Test Examples

Water emulsions of lubricating agents comprising 85 weight % of the processing agents shown in Table 1 and 15 weight % of POE nonylphenyl ether were prepared.

5 Test yarns were prepared by applying these water emulsions to acrylic filament yarns (75 denier/40 filaments) so that 0.5 ± 0.1 weight % will be deposited on each by the kiss roll method, and the coefficients of friction and generation of static electricity were
10 measured and evaluated by the method to be described.

In addition, the aforementioned water emulsions were applied to acrylic filament yarns (16000 denier/12000 filaments) at the rate of 0.5 ± 0.1 weight % by immersion method. The yarns were then dried for 4
15 seconds at 115°C by means of a dry heat roller to prepare a precursor tow and this was used as sample to evaluate the filament separability by the method described below.

Furthermore, the precursor tow was processed for 60
20 minutes inside an oven of forced circulation type at 240°C to obtain infusibilized fibers and they were used as samples to evaluate their infusibility by the method to be described later.

Measurement of the coefficient of friction

The sample was left for 24 hours under the condition of 20°C and 65%RH and caused to run in contact with a cylindrical chromium-plated pin under the same conditions with initial tension 20 g and yarn velocity of 100m/min. Coefficient of friction was measured by using a μ -meter (made by Eiko Sokki-sha). The lower the measured value, the better is the result.

Evaluation of static electricity

Concurrently with the aforementioned measurement of coefficient of friction, electrostatic voltage of the yarn after the contact with the chromium-plated pin was measured by means of a static electrometer (made by Kasuga Denki Kabushiki Kaisha) and the results were evaluated according to the following standards:

0 : Voltage less than 100V

1 : Voltage 100V to less than 300V

X : Voltage 300V or greater

Filament Separability

The sample was cut to 2cm lengths and shaken lightly over a black sheet of paper and its opening property of

each filament was evaluated according to the following standards:

00 : Separability very good

0 : Good

5 1 : Bad

X : Very bad

Infusibility

10 The sample was cut to 2cm and shaken lightly over a white sheet of paper and its infusibility was evaluated according to the following standards:

00 : No fusion

0 : Very little fusion

1 : Some fusion

X : Fusion to a considerable degree

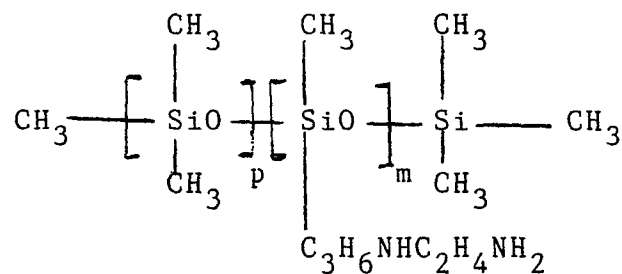
15 The results are shown in Table 1. One can clearly see from these results that the lubricating agents of the present invention provide superior filament separability and infusibility which are necessary properties of any lubricating agent for the production
20 of carbon yarns, in addition to other superior characteristics such as lubricity, antistatic capability etc.

Table 1

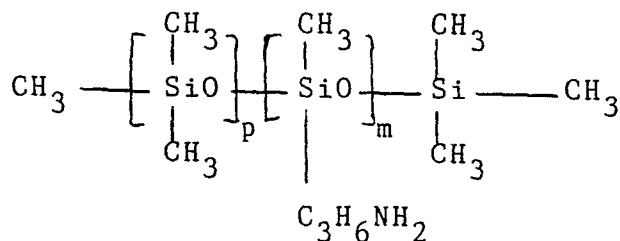
		Coef.	Vol.	Sep.	Inf
Test Examples:					
5	1 Amino polysiloxane (A)	0.275	0	00	00
	1400cst, N=0.2%				
	2 Same as above	0.284	0	00	00
	9000cst, N=0.2%				
	3 Same as above	0.290	0	0	0
	18000cst, N=0.2%				
10	4 Same as above	0.279	0	0	0
	2000cst, N=0.8%				
Comparison Examples:					
	1 Amino polysiloxane (A)	0.270	0	X	X
	200cst, N=1.4%				
15	2 Amino polysiloxane (B)	0.300	1	1	1
	1000cst, N=0.4%				
	3 Dimethyl polysiloxane	0.306	X	1 to X	1 to X
	1000cst				
	4 Polyether polysiloxane	0.317	0	X	X
20	3700cst				
	5 Epoxy polysiloxane	0.304	X	X	X
	100cst				
	6 POE(10) lauryl ether	0.268	0	1 to X	X
	7 Lauryl trimethyl				
25	ammonium chloride	0.290	0	1 to X	X

where cst is the viscosity at 25°C in centistokes, N is the nitrogen content in weight %, amino polysiloxane (A) and (B) are as shown below wherein p and m are the same as in formula (I):

5 Amino polysiloxane (A):



Amino polysiloxane (B):

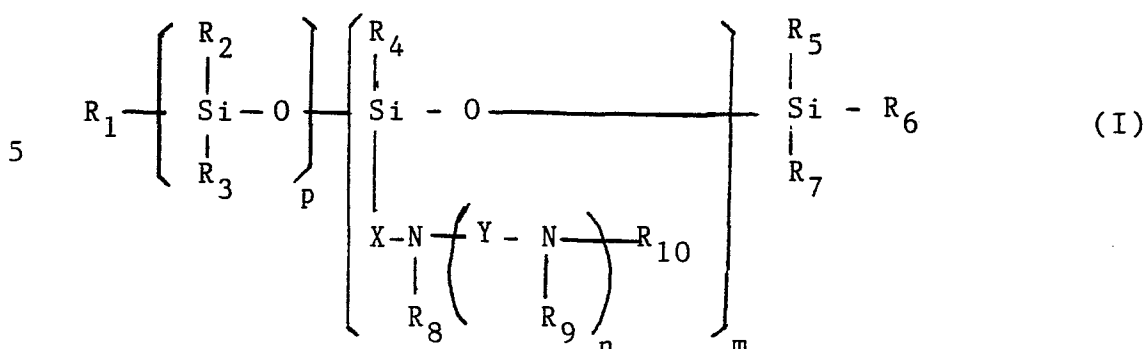


and

- 10 Coe = Coefficient of friction
 Vol = Evaluation of electrostatic voltage
 Sep = Evaluation of filament separability
 Inf = Evaluation of infusibility

CLAIMS:

1. A lubricating agent for use in the production of carbon yarns comprising at least one amino polysiloxane of formula (I)



(where X represent an alkylene group with 3 to 5 carbon atoms, Y represent an alkylene group with 2 to 6 carbon atoms or a phenylene group, R_1 and R_3 each represents a hydrogen atom, an alkyl group with 1 to 5 carbon atoms or a phenyl group, R_2 and R_4 each represent a methyl group or an ethyl group, R_5 , R_6 and R_7 each represent a hydrogen atom, a methyl group or an ethyl group, m is 1, n is an integer equal to or greater than 1 and p is 0 or an integer in the range of 1 to 5, as effective component, the nitrogen content of said effective component being 1 weight % or less.

2. A lubricating agent according to claim 1, wherein the viscosity at 25°C of said effective component is 100 to 10000 centistokes and the nitrogen content of said effective component is 0.5 weight % or less.

5 3. A lubricating agent according to claim 1 or claim 2, containing an effective component of formula (I) in which R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and R_7 are all methyl groups.

4. A lubricating agent according to claim 3, containing
10 an effective amount of a component of formula (1) in which X represents a propylene group, Y represents an ethylene group, R_8 , R_9 and R_{10} each represent a hydrogen atom and n is 1.

5. A method of lubricating yarns used in the
15 manufacture of carbon yarns, comprising applying thereto a lubricating agent according to any of claims 1 to 4.



European Patent
Office

EUROPEAN SEARCH REPORT

0157499

Application number

EP 85 30 1397

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-4 080 417 (S. KISHIMOTO) * Claims 1,3,16,17,19 * ---	1-5	D 01 F 9/22 D 01 F 9/14 D 06 M 15/00
X	US-A-4 009 248 (S. KISHIMOTO) * Claims 1-3,6,11,12 * ---	1-5	
X	GB-A-2 059 407 (SUMITOMO) * Claims 1,4; page 5, example 1 * ---	1-5	
X	GB-A-2 041 901 (SUMITOMO) * Claims 1,2 * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 G D 01 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03-07-1985	Examiner DEPIJPER R.D.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	